Reviews

Metallacumulenes as Potential Electron Reservoir Devices

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This paper reviews recent work in the area of organomanganese chemistry whose purpose is the design of single-molecule components for electronics. This field has recently received much attention in the pursuit of continued miniaturization of electronics. Electron reservoirs and molecular wires are basic motifs of single-electron devices. Both can accept and release electrons in a reversible fashion, but the former can also store electrons. Our recent work in the field deals with complexes of two distinct types: mononuclear half-sandwich manganese(I) vinylidene complexes, designed for application as electron reservoirs, and half-sandwich dinuclear manganese complexes and the bis-dmpe dinuclear Mn^{II}/Mn^{II} compounds, which were designed to serve as molecular wires. However, this review will focus on the mononuclear half-sandwich manganese(I) vinylidene and butatrienylidene systems, which have been synthetically successful systems and are supported by extensive DFT calculations and further detailed investigations using NMR, IR, UV−vis, and Raman spectroscopy, CV, magnetic susceptibilities, and X-ray diffraction studies.

Introduction

Molecular electronics can be defined as technologies utilizing single molecules, small groups of molecules, carbon nanotubes, or nanoscale metallic or semiconductor wires to perform electronic functions.[1−5] Some have defined it as technologies utilizing only single molecules, but this definition is far too limiting. From the broader definition, it can be suggested that any device utilizing molecular properties is a molecular electronic device.[4] A molecular level device can be defined as an assembly of a discrete number of molecular components designed to achieve a specific function. A promising strategy toward technology at the nanometer scale is offered by the small-upward (bottom-up) approach,[6−9] which starts from atoms or molecules and builds up to nanostructures. The search for individual molecules that would behave as electrical switches began in 1974, with the pioneering work of Aviram and Ratner,[10−12] who proposed a theory on molecular rectification. Tour et al. have synthesized the spiro switch proposed by Aviram, and different variants of the molecular rectifier have been made.[13,14] Much work has been done to measure the conductance and other electrical properties of individual molecules or to model them.[15,16] However, the major part of this field has centered on organic systems, and these systems are sometimes plagued by the inability to withstand high operation temperatures. Systems involving transition metals can play a very crucial role in this area. Apart from temperature stability, organometallic systems can be fine-tuned by varying the metal centers, since the energy of the overall system predominantly is determined by the metal center. In other words, one manipulates the HOMO and LUMO of the molecules and, as a consequence, their absolute hardness and electronegativity.[17] The simplest of devices encompassing the molecular device, as one would envisage, are one for storing electrons and the other for conducting electrons. The former device can be termed a molecular battery and the latter a molecular wire.[18]

The electron-transfer process,[19] which is known to play a key role in supramolecular chemistry, biochemistry, and molecular

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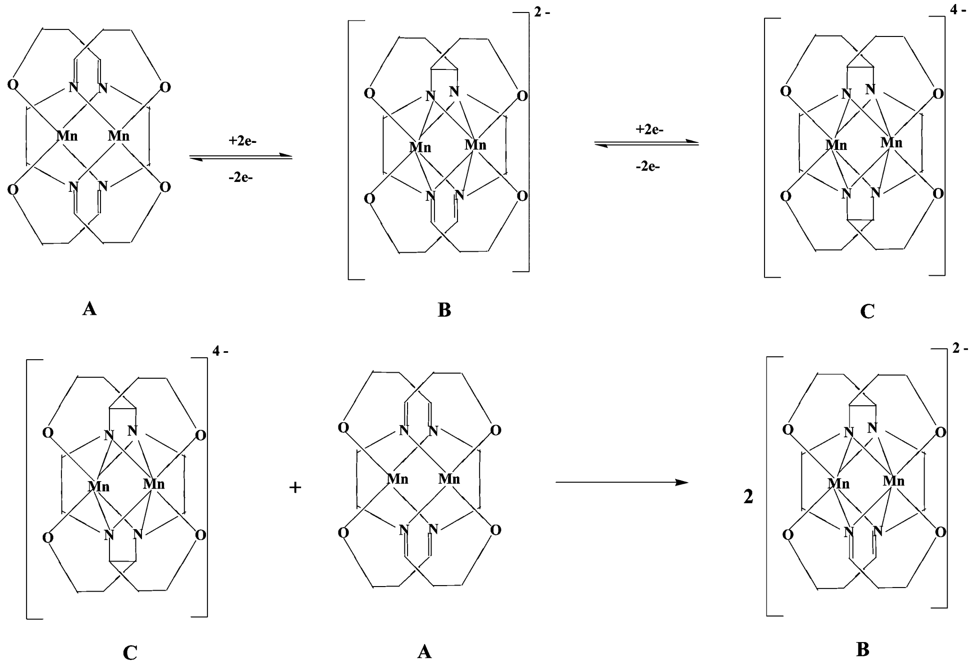
Scheme 1



activation, is also a key point in the field of organometallic molecular devices. In the context of molecular devices, electron reservoirs are basic motifs of a single-electron device, which can store and release electrons in a reversible fashion, and thereby they form crucial components of such devices. The concept of "organometallic electron reservoir" was defined and based on the fact that organometallic complexes are able to store energy in the form of one or several electrons. Previously, Astruc and co-workers have reported systems[20−22] in which the electrons are stored and released from a ferrocene model based system. However, the redox chemistry in most of the systems reported was either metal- or ligand-centered until Floriani and co-workers reported[23−32] a system whereby the C−C bond was utilized for storing and releasing electrons. The mechanism involved an oxidative coupling and a reductive decoupling process. Many cases are known which operate in at least one direction, except for Floriani's electron-rich manganese(II) systems derived from the stepwise reduction of the model compounds [Mn(salophen)(thf)$_2$] and [Mn(3,5-^{t}Bu$_4$salophen)(thf)]$_2$, which operate in both directions.

Such a redox process is shown pictorially in Scheme 1, where complex **A** undergoes a stepwise reduction to **B** and **C** upon reaction with sodium metal in THF. The introduction of the two electrons into the dimer causes the reductive coupling of two imino groups across the two monomers with subsequent formation of a C−C bond. The C−C bond formation is accompanied by a change in the bonding mode of the salophen skeleton. The further introduction of two electrons leading from **B** to **C** has the same effect on the other pair of imino groups. **B** could be regenerated by mixing equimolar amounts of **A** and **C**. Unfortunately, very rarely does the redox chemistry of ligands in complexes have chemical consequences such as the formation or cleavage of bonds, and even more rarely is the process reversible.

During the past decade our research efforts have been focused on the design and synthesis of molecules that are imprinted with the functions of a molecular battery or a molecular wire. The systems we pursued were centered on the utilization of very electron rich manganese centers as the redox part of the molecule. We believe that the manganese center holds the key information for these molecules that imparts low-energy work function characteristics into these molecular systems. We wish to bring forth and reiterate the importance and uniqueness of the manganese metal in these systems throughout this review.

In this review we focus on our recent work concerning the chemistry of metallacumulenes, a class of molecules that has been investigated in depth for applications as molecular batteries. Metallacumulenes, M(=C)$_m$CR$_2$, are of considerable interest from several perspectives.[33−37] In the context of materials science, π-conjugated linear (=C)$_m$ moieties fundamentally allow communication between metal centers and remote functional groups and, therefore, could be potentially useful as nonlinear optical materials and molecular wires.[38−42] Metallacumulenes also represent an interesting class of metal−carbon multiple-bonded compounds for the study of the bonding interactions in M(=C)$_m$CR$_2$, particularly with regard to the

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degree of π-bonding/back-bonding interactions[43−59] and π delocalization effects. In addition to the theoretical interest in such complexes, the high degree of unsaturation in these metallacumulene complexes $L_nM(=C)_mCR_2$ also became a challenge for preparative endeavors.[55,60−65] Metallacumulenes with $m = 1, 2$ (vinylidenes or allenylidenes) are very common and have been thoroughly studied in recent years.[45,46,48,59,66−76] Complexes with $m = 4$ are less common, but some examples of such complexes are known.[77−83] However, species with a four-carbon chain ($m = 3$) appeared to be of extraordinarily low stability and therefore have been accessed only rarely. In situ preparations of cationic species containing a $[Ru=C=C=C=CRH]^+$ unit were reported, R = H by Bruce[80−82] and R ≠ H by Dixneuf[84] and Winter,[77,78,85] but the $Ru(=C)_4$ species were quite short-lived, preventing spectroscopic characterization. Lapinte's group managed to stabilize a peculiar complex containing an $Fe(=C)_4$ cumulenic motif by attaching an $FeCp^*(CO)_2$ moiety to the terminal carbon atom of the cumulenic chain.[83] Recently, Werner's group prepared the first stable neutral C_4 metallacumulene compound containing a $Ir=C=C=C=CPh_2$ unit[44,86] and also have later reported reactivity studies of this complex.[43,44]

The two major types of complexes we have particularly studied in the last few years for application as molecular batteries are manganese vinylidene complexes ($m = 2$) of the type $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2)(=C=CR^1R^2)$[87,88] and manganese butatrienylidene complexes ($m = 4$) of the type $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2)(=C=C=C=CR^1R^2)$.[89,90] We believe that our systems are unique in the sense that both the metal center and the ligand work in conjunction with each other. The ligand systems, vinylidene and butatrienylidene in our case, have been known for decades and are easily accessible by many routes. Nevertheless, species of the type $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2)(=C=CR^1H)$, for example, were designed and synthesized for the purpose. The auxiliary phosphine ligands, the substituents on the C_β atom, and the cyclopentadienyl ligand play a crucial role in the redox properties of these complexes. This system stores and releases electrons from a C−C bond in a fashion that is unprecedented, utilizing the oxidative coupling and reductive decoupling processes. One could certainly envisage the possibility of utilizing this process of formation and cleavage of chemical bonds for the purpose of a molecular battery, since two complementary electron-storage and -releasing units are the fundamental constituents of storage cells.

Mononuclear Half-Sandwich Manganese Complexes

Several methods have been employed for the preparation of mononuclear vinylidene complexes: from 1-alkynes via a formal

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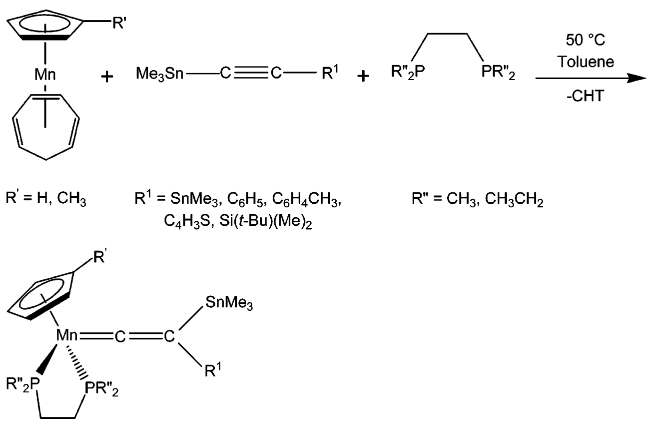
1,2-hydrogen shift,[65,88,91−108] by addition of electrophiles to metal alkynyl complexes,[109−111] by deprotonation of carbyne complexes,[112,113] and by formal dehydration of acyl complexes.[114−117] In addition, alkenes, preformed vinyl complexes, and disubstituted alkynes have been used as precursors in a variety of transformations.[95,118−123] Transfer of vinylidene ligands between metal centers[97,124] and modification of existing vinylidene ligands[97,124,125] are reactions which also deserve further investigation.

Recently, the diamagnetic Mn(I) vinylidene complexes Mn(dmpe)(η^5-C_5H_4Me)(=C=CRH) (R = Ph, $SiMe_3$) were prepared in our group by addition of $H^\bullet$ atoms to toluene solutions of the corresponding d^5 Mn(dmpe)(η^5-C_5H_4Me)(C≡CR) complexes.[126] These species were labile and showed a great tendency to undergo carbon-centered reactions such as hydrogen abstraction and radical coupling. These processes were competitive, producing the mononuclear vinylidene complexes or the binuclear complexes. The course of these transformations was strongly dependent on the nature of R and the solvent: i.e., the ability of any of these components to donate a hydrogen radical. When Mn(dmpe)(η^5-C_5H_4Me)(C≡CR) was reacted with n-Bu_3SnH as the $H^\bullet$ source, we observed the formation of the $H^\bullet$ scavenging products in 83% yield. As byproducts the $SnBu_3$-substituted vinylidene complexes Mn(dmpe)(η^5-C_5H_4Me)(=C=C(R)$SnBu_3$) also were identified spectroscopically. A complete separation of these complexes from the other products could not be achieved by fractional crystallization or by chromatography. However, this byproduct formation was circumvented by applying Mo(η^5-C_5Me_5)$(CO)_3H$ as a $H^\bullet$ source. In this case the products were obtained in quantitative yield, but still the whole process involved too many steps. Obviously, we were interested in synthesizing these vinylidenes in a more straightforward and facile way.

Scheme 2



(a) Synthesis of Mononuclear Half-Sandwich Manganese Vinylidene Complexes. Another easily accessible method to obtain metal vinylidene complexes, which was of particular interest to us, involves the addition of acetylene derivatives to coordinatively unsaturated metal complexes.[33] From this point of view, we believed that the Mn^I complex Mn(η^5-C_5H_4R')(η^6-cycloheptatriene) (R′ = H, CH_3)[127] would be an excellent starting material for the preparation of manganese vinylidene species, due to the labile character of the Mn−heptatriene interaction, which makes this ligand easily substitutable by other strong electron donors such as phosphines and acetylenes.[128] Electron-rich systems such as d^6 systems favored the formation of the vinylidene over the acetylene complexes, although the latter are intermediates in the formation of the vinylidene species. Since earlier reports by Terry et al.[129] indicated that vinylidene complexes of the type Mn(C_5H_5)$(CO)_2$(=C=C$(H)_2$) were thermally unstable and thus were only generated and studied at low temperature, we decided to use bidentate phosphane ligands, $Me_2PCH_2CH_2PMe_2$ (dmpe) and $Et_2PCH_2CH_2PEt_2$ (depe), to obtain isolable compounds that are thermally stable.

The reaction of Mn(C_5H_4R')(η^6-cycloheptatriene) (R′ = H, CH_3) with various trimethyltin-substituted acetylenes

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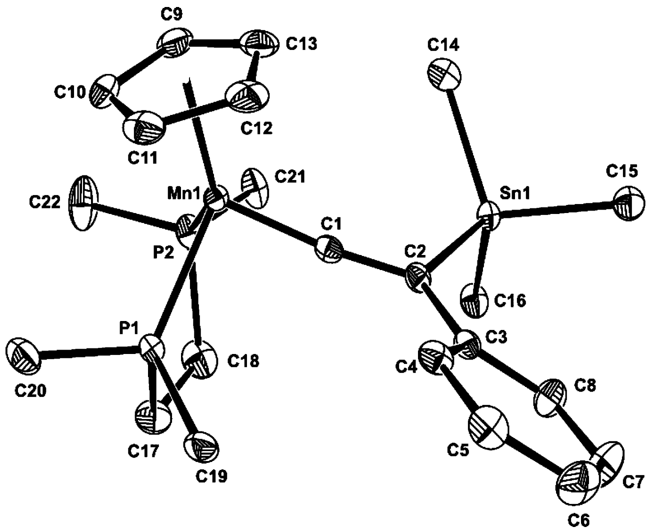
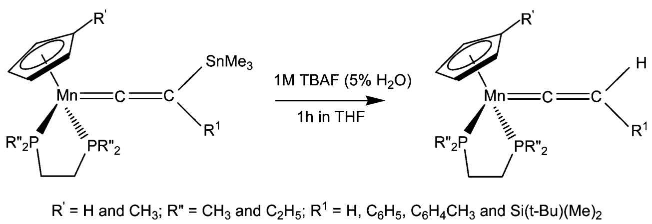


Figure 1. Molecular structure of $Mn(C_5H_5)(Me_2PCH_2CH_2PMe_2)({=}C{=}C(SnMe_3)(C_6H_5))$ (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mn1−C1 = 1.761(6), C1−C2 = 1.344(8), C2−Sn1 = 2.139(6), Mn1−P1 = 2.1895(17), Mn1−P2 = 2.1877(17); Mn1−C1−C2 = 172.9(5), C1−C2−Sn1 = 115.2(4), C1−C2−C3 = 123.8(5), C3−C2−Sn1 = 120.9(4). All hydrogen atoms have been omitted for clarity.

$R^1C{\equiv}CSnMe_3$ (R^1 = $SnMe_3$, C_6H_5, C_4H_3S, CH_3, $C_6H_4CH_3$) and $R''_2PCH_2CH_2PR''_2$ (R'' = CH_3, C_2H_5) quantitatively yielded at 50 °C after 3 h a wide range of vinylidene complexes of the type $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2)({=}C{=}CR^1SnMe_3)$, as shown in Scheme 2.[88] In addition to full spectroscopic characterization, the complexes $Mn(C_5H_5)(dmpe)({=}C{=}C(SnMe_3)_2)$ and $Mn(C_5H_5)(dmpe)({=}C{=}C(SnMe_3)(C_6H_5))$ were structurally characterized by X-ray diffraction.[87,88] As a representative example, the X-ray structure of the latter complex is shown in Figure 1. It was quite surprising that related reactions could not be accomplished with terminal acetylenes, in contrast to, for instance, the reported syntheses of “nonsubstituted” vinylidene rhodium complexes.[130,131] Apparently the replacement of the tin group with the parent H causes an insurmountable kinetic barrier in the acetylene/vinylidene rearrangement process. The acetylene/vinylidene rearrangement in electron-rich systems is normally considered to be a multistep process, with initial acetylene coordination to the metal center, then oxidative addition of the terminal ≡CH bond, and finally migration of the metal-bound H to the β-carbon atom. Very often, in more electron-poor systems the rearrangement follows a deprotonation/protonation sequence, where the initial acetylene complex is deprotonated and the acetylide complex thus formed is protonated. In electron-rich systems, the oxidative addition reactions as well as any hypothetical deprotonation reactions might have a high kinetic barrier. These barriers are apparently reduced when the terminal substituent of the acetylene group is a tin-containing group. General mechanistic aspects regarding the formation of metal vinylidenes from alkynes have been reviewed by Wakatsuki.[132]

Even though there has been no quantitative theoretical study of this phenomenon, it is presumed that either the organotin-containing acetylene/vinylidene rearrangement follows an intramolecular, more or less concerted pathway, in which the organotin group moves as the μ_2-acetylene moiety “rises up” for the μ_1 binding mode, or the whole reaction sequence follows a solvent-caged radical pathway with involvement of $R_3Sn^{\bullet}$ radicals. If by some means the organotin groups of the vinylidene complexes could be replaced by a H substituent, the organotin vinylidene complexes could be considered as synthetic intermediates for the access to the H vinylidenes, thus circumventing the kinetically unaccessible acetylene/vinylidene rearrangement and providing a pathway with lower energy barriers. Indeed, the reactions of the species $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2)({=}C{=}CR^1SnMe_3)$ (R' = H, Me; R'' = Me, Et; R^1 = H, C_6H_5, C_6H_4Me, $Si(t\text{-}Bu)Me_2$) complexes with 1 equiv of $[Bu_4N]F$ (containing 5% H_2O) removed the organotin groups, giving the parent vinylidene species $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2)({=}C{=}CR^1(H))$ (Scheme 3). The structures of $Mn(C_5H_5)(dmpe)({=}C{=}CH_2)$ (shown in Figure 2),[87] $Mn(C_5H_5)(dmpe)({=}C{=}C(H)(C_6H_5))$,[88] $Mn(C_5H_5)(dmpe)({=}C{=}C(H)(C_4H_3S))$,[88] and $Mn(C_5H_5)(depe)({=}C{=}CH_2)$[133] were confirmed by X-ray diffraction analyses. The complexes $Mn(C_5H_5)(dmpe)({=}C{=}CH_2)$ and $Mn(C_5H_5)(depe)({=}C{=}CH_2)$ constitute the finest examples of thermally stable half-sandwich Mn(I) vinylidene complexes with phosphine ligands and two H atoms on the C_β atom. This fact points out the pivotal role of the phosphine ligand influence on the stability of these manganese complexes.

Scheme 3



(b) Oxidative Coupling of Manganese Vinylidene Complexes. These newly formed complexes are highly oxygen sensitive, indicating low-energy work functions for their HOMO

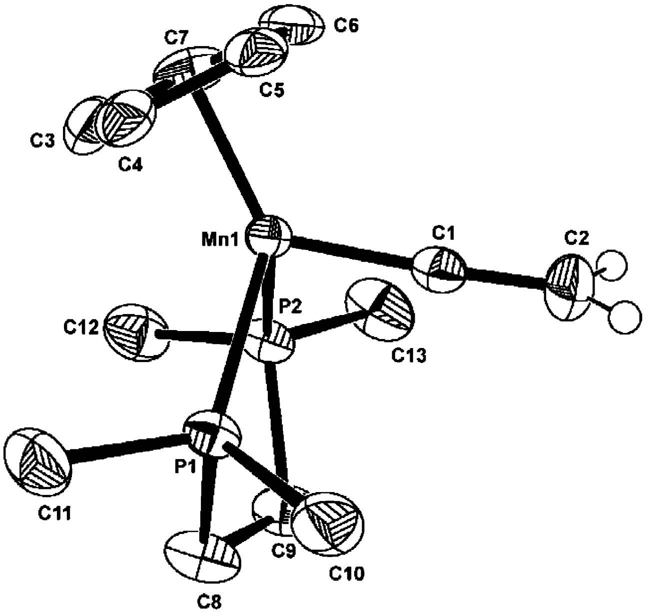


Figure 2. Molecular structure of $Mn(C_5H_5)(dmpe)({=}C{=}CH_2)$ (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Mn1−C1 = 1.755(3), C1−C2 = 1.316(4); C2−C1−Mn1 = 176.6(3). Selected hydrogen atoms are omitted for clarity.

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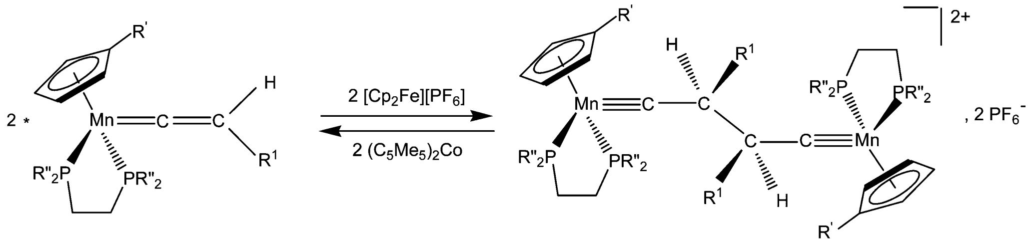
Scheme 4



R' = H, R" = C_2H_5, R^1 = H, C_6H_5 and C_4H_3S; R' = Me, R" = Me, R^1 = H, C_6H_5 and C_4H_3S

electrons. Indeed, oxidation of the vinylidene complexes Mn(C_5H_5)(depe)(=C=CR^1(H)) and Mn(C_5H_4Me)(dmpe)(=C=CR^1(H)) (R^1 = H, C_6H_5 and C_4H_3S) with the mild oxidant [Cp_2Fe][PF_6] (1 equiv) in CH_2Cl_2 yielded after 1 h the corresponding dinuclear carbyne complexes [Mn]≡CC(R^1)(H)C(R^1)(H)C≡[Mn]·2PF_6 (Scheme 4). In the cases of Mn(C_5H_5)(depe)(=C=CR^1(H)) and Mn(C_5H_4Me)(dmpe)(=C=CR^1(H)) (R^1 = C_6H_5, C_4H_3S) oxidation gave specifically the meso (*R*,*S*) diastereomers, of which (C_5H_4Me)(dmpe)Mn≡CC(R^1)(H)C(R^1)(H)C≡[Mn]·2PF_6 (R^1 = H, C_6H_5) have been characterized spectroscopically and unequivocally established by X-ray crystallographic studies.[87,88] This selectivity might arise from an appropriate sterically enforced transition state of the dimerization process, which is assumed to involve a radical cation of the type [(C_5H_4R′)(R″$_2$PCH_2CH_2PR″$_2$)Mn=C=C(R^1)(H)$^{\bullet+}$.

The assumption that the selectivity arises from an appropriate sterically enforced structure of the radical cation that appears during the dimerization process was confirmed by DFT calculations performed on the dinuclear model products [(C_5H_4Me)(dHpe)Mn≡CC(H)(R^1)C(H)(R^1)C≡Mn(dHpe)(C_5H_4Me)]$^{2+}$ (R^1 = Me, C_6H_5) bearing $H_2PCH_2CH_2PH_2$. Full geometry optimizations carried out for both configurations of the complexes led to differences in energy between the true minima of the dinuclear species in favor of the *R*,*S* diastereomers by 1.1 and 4.6 kcal/mol for compounds with R^1 = Me, C_6H_5, respectively. This thermodynamic preference is assumed to show up also to some extent in the energies of the transition states, which would allow the *R*,*S* isomers to form more quickly.

However, in some cases, such as in Mn(C_5H_4R′)(dmpe)(=C=CR^1(H)) (R′ = H, R^1 = H, C_6H_5, C_6H_4Me, C_4H_3S; R′ = Me, R^1 = Si(*t*-Bu)Me_2)) and Mn(C_5H_4R′)(depe)(=C=CR^1(H)) (R′ = H, R^1 = C_6H_4Me; R′ = Me, R^1 = H, C_6H_5, C_6H_4Me, C_4H_3S), oxidation led to a mixture of complexes, one of them being the coupling product. The other complexes in the mixture were identified as the dehydrogenative coupling product [(C_5H_4R′)(R″$_2$PCH_2CH_2PR″$_2$)Mn≡CCR^1=CR^{1}C≡Mn(R″$_2$PCH_2CH_2PR″$_2$)(C_5H_4R′)] and the carbyne complex [(C_5H_4R′)(R″$_2$PCH_2CH_2PR″$_2$)Mn≡CCH_3][PF_6]. We believe that these differences in the products obtained arise from the difference in the oxidation potentials of the vinylidene complexes as one decisive factor. An overly small difference in the potentials between the vinylidene and the oxidizing agent may cause a redox process that is too slow. Other specific factors for retardation of such processes might be steric influences. Oxidation of the starting vinylidene complex by [$FeCp_2$][PF_6] that is too slow leaves the radical cation of vinylidene species enough time to undergo proton transfer to the residual vinylidene complex, which can act as a base and form the generally quite stable carbyne complexes. The remaining Mn(II) species (C_5H_4R′)(R″$_2$PCH_2CH_2PR″$_2$)Mn−C≡CR^1, being radicals as well, undergo self-coupling to the μ-vicinal alkylidene type bridged compounds (vide infra).

Redox-activated processes of dimerization or dehydrodimerization of transition metals are frequently used for the synthesis of such binuclear compounds. Green and co-workers observed that oxidation of the anionic metal vinylidene complex [Li][Cp*(P(OMe)$_3$)$_2$M=C=CH*t*Bu] resulted in a dimerization to form the neutral product [Cp*(P(OMe)$_3$)$_2$M≡CCH*t*Bu]$_2$.[112] Oxidation of the vinylidene complexes [Li]Tp′(CO)$_2$M=C=CH_2 (M = Mo, W) with a ferrocenium salt, iodine, or nitrobenzene gave high yields of [M]≡CCH_2CH_2C≡[M].[134] Oxidative dehydrodimerization studies of the vinylidene complexes Cp*(CO)$_2$Mn=C=CHPh,[135] Cp(CO)(PPh_3)Mn=C=CHPh,[135] and Cp(CO)$_2$Re=C=CHPh[136] showed two competitive routes of coupling via the radical cation intermediate, one of which leads by C−C coupling to the bis-carbyne dication. One-electron reduction of the Fischer-type carbene complex (OC)$_5$W=C(Ph)(OMe) reported by Iwasawa et al. gave the anion radical (OC)$_5$W=C(Ph)(OMe)$^{\bullet-}$, which dimerized to give the dianion complex [(OC)$_5$W−C(Ph)(OMe)(Ph)(OMe)C−W(CO)$_5$]$^{2-}$ as an intermediate of the reaction.[137] Some other examples of oxidative or reductive coupling reactions of vinylidene complexes have been reported in the literature; nevertheless, none of them showed a reversible process to regenerate the initial mononuclear compound.

The uniqueness of our systems lies in the fact that the reduction of the dinuclear carbyne complexes presented in Scheme 4 with Cp_2*Co yielded quantitatively the corresponding mononuclear vinylidene complexes. The cyclic voltammetric studies performed for the complexes Mn(C_5H_4Me)(dmpe)(=C=CH_2) and Mn(C_5H_4Me)(dmpe)(=C=C(C_6H_5)H) showed a quasi-reversible behavior. The first oxidation step is a relatively slow step at −0.246 V, but the dimerization occurs very rapidly and was observed at 0.368 V. Further, the dinuclear complexes can be re-reduced, and thus, the whole process turns out to be quasi-reversible.

(c) Reversible C−C σ-Bond Formation: a DFT Study. On the basis of molecular orbital calculations performed at the semiempirical level on the d^6-electron metal complexes [CpFe(CO)$_2$(=C=CH_2)]$^+$, [CpFe(PH_3)$_2$(=C=CH_2)]$^{+,}$ and CpMn(CO)$_2$(=C=CH_2)[138,139] and additionally on d^8-electron IrCl(PH_3)$_2$(=C=CH_2),[140] the frontier orbital interactions between the metal fragment and its vinylidene ligand have been examined. A simplified interaction diagram has been recently proposed by Wakatsuki[132] from these early studies as an

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introduction to mechanistic studies of alkyne to vinylidene tautomerization. Only a few theoretical investigations have been performed at the DFT level on the transition metal vinylidene complexes in recent years. Most of the reported studies focused on the tautomerization between free acetylene (HC≡CH) and vinylidene (:C=CH$_2$) occurring in the coordination sphere of transition metals.[132,141−144] Possible mechanisms such as those proceeding through a direct 1,2-hydrogen shift or through a hydrido−alkynyl intermediate were detailed and compared on the basis of calculated potential energy surfaces, including equilibrium structures and transition states. Some other groups proposed an overall view of metallacumulenes of the type $L_nM(=C)_nR_2$ for information between the simplest and the long-chain complexes: their electronic structure (even-membered chain vs odd-membered chain cumulenes), their bonding (dissociation energies for the metal-cumulene bond), and their reactivity (electrophilic or nucleophilic character of the carbon atoms).[54,145−147] Recent studies on $MR^1Cl(C=CHR^2)(L_2)$ complexes (M = Ru, Os; R^1 = H, CHCMe$_3$, Cl, etc.; R^2 = Ph, SiMe$_3$,etc.; L = phosphine) indicated also that the π-accepting substituents R^1 and R^2 would reduce the rotational barrier in vinylidene, while the barrier would increase with the increasing π-accepting ability of phosphines.[148,149]

The experimental contribution brought to the field of metal vinylidene complexes by the novelty of our experimental results was also supported by density functional calculations.[87,88] Indeed, to investigate the role of substituents on the C_β atom in the described coupling process leading to dinuclear manganese systems, a theoretical study was performed on the cationic model systems $[(C_5H_4Me)(dHpe)Mn=C=CHR^1]^+$ (R^1 = H, Me, C_6H_5, $C_6H_4CH_3$, Si(*t*-Bu)(Me)$_2$) and the corresponding binuclear biscarbyne complexes $[(C_5H_4Me)(dHpe)Mn\equiv CCHR^1CHR^1C\equiv Mn(dHpe)(C_5H_4Me)]^{2+}$, for which the $H_2PCH_2CH_2PH_2$ (dHpe) ligand has been used instead of the dmpe ligand. In the selected molecules only the dimer complexes with R^1 = H, C_6H_5 have been formed and experimentally characterized without ambiguity, while the reaction starting from complexes with R^1 = C_6H_4-Me, Si(*t*-Bu)(Me)$_2$ led to complicated mixtures. The optimized mononuclear cationic radical systems showed spin densities located at the manganese and the C_β atoms. The probability of finding the unpaired electron of the system on the terminal carbon atom C_β decreases in the order R^1 = H (+0.367α) > Me (+0.366α) > C_6H_5 (+0.358α) > $C_6H_4CH_3$ (+0.344α) > Si(*t*-Bu)(CH$_3$)$_2$ (+0.332α). Furthermore, single-point calculations including a model for solvation effects performed on the gas-phase geometries of the mononuclear and dinuclear model complexes led to dimerization energies ΔE of −24.2 (R^1 = H), −12.3 (Me), −3.9 (C_6H_5), −2.1 (C_6H_4Me), and +12.1 kcal/mol (Si(*t*-Bu)(Me)$_2$), following the same order as the C_β spin density ($\Delta E = E_{\text{dimer}} - 2E_{\text{monomer}}$). Transposed also into kinetics, these calculations suggest that the dimerization process to generate a C−C-coupled dinuclear product should be easiest for $[(C_5H_4Me)(dHpe)Mn=C=CH_2]^+$ and is even not possible at the other end of the series $[(C_5H_4Me)(dHpe)Mn=C=CH(Si(t\text{-Bu})(CH_3)_2)]^+$, which is in very good agreement with the experimental observations. Nevertheless, for all studied systems the negative dimerization energies indicate that the formation of the dinuclear compounds is thermodynamically favored and, consequently, we believe that such reactions can be tuned toward formation of a single product by using kinetically fast, powerful oxidizing agents. These kinds of studies are currently being investigated. It is worth mentioning from the X-ray diffraction studies of $[(C_5H_4Me)(dmp)Mn\equiv CCH_2CH_2C\equiv Mn(dmpe)(C_5H_4Me)][PF_6]_2$ and $[(C_5H_4Me)(dmpe)Mn\equiv CCHPhCHPhC\equiv Mn(dmpe)(C_5H_4Me)][PF_6]_2$ that the $C_\alpha-C_\beta$ bonds are, at 1.463(4) and 1.493(6) Å, on the short side of a C−C single bond, presumably reflecting a residual double-bond character, while the newly formed $C_\beta-C_{\beta'}$ bonds at 1.509(6) and 1.503(9) Å would correspond to “real” single bonds.[87,88]

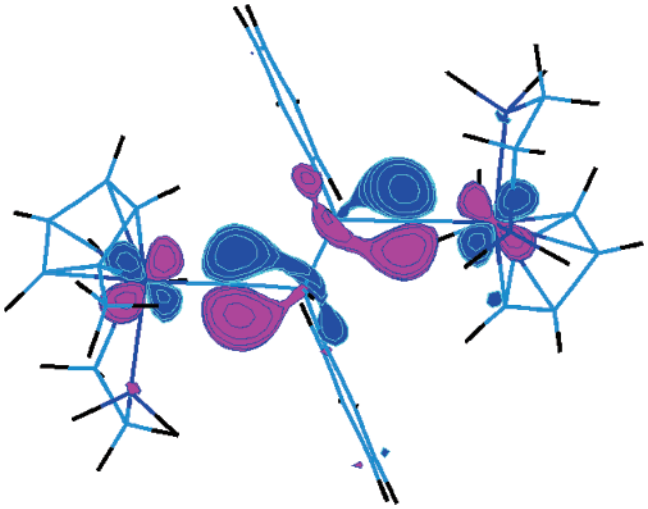

Figure 3. Calculated LUMO of the dinuclear model complex $[(C_5H_4Me)(dHpe)Mn\equiv CCHPhCHPhC\equiv Mn(dHpe)(C_5H_4Me)]^{2+}$ showing the π-type antibonding interactions between Mn and C_α and between C_β and $C_{\beta'}$.

The reversibility of this process can be explained and is highlighted by the shape of the LUMO of the low-spin dinuclear model complex $[(C_5H_4Me)(H_2PCH_2CH_2PH_2)Mn\equiv CCHPhCHPhC\equiv Mn(H_2PCH_2CH_2PH_2)(C_5H_4Me)]^{2+}$ (Figure 3). The vacant orbital is mainly of π-type antibonding character between Mn and C_α and of σ-antibonding character between C_β and $C_{\beta'}$. The reduction of the dinuclear compound resulting formally from an addition of two electrons into the LUMO destabilizes the Mn≡C_α and the $C_\beta-C_{\beta'}$ bonds and leads back to the mononuclear vinylidene systems. Single-point calculations on the gas-phase geometries with a model for solvation effects performed on the selected dinuclear model complexes gave the energy level of the corresponding LUMO at −5.26 (R^1 = H), −5.14 (Me), −4.85 (C_6H_5), and −4.75 (C_6H_4Me). The energy difference between the HOMO and the LUMO (low differences correspond to soft molecules, low absolute hardness)[17] follows the same order with $\Delta E_{\text{HOMO-LUMO}}$ = 2.16 (R^1 = H), 2.18 (Me), 2.29 (C_6H_5), and 2.33 ($C_6H_4CH_3$) to indicate that the reduction of the dinuclear carbyne complexes should be the easiest in the case of R^1 = H, because the LUMO in this case is more accessible to the addition of two electrons. The complex $[(C_5H_4Me)(dHpe)Mn\equiv CCH(Si(t\text{-Bu})(Me)_2)CH(Si(t\text{-Bu})(Me)_2)C\equiv Mn(dHpe)(C_5H_4Me)]^{2+}$ should be treated separately from the others, because it seems clear that the very positive dimerization energy of ΔE = +12.1 kcal/mol is not of electronic origin but, rather, is due to the very bulky ligand Si(*t*-Bu)(Me)$_2$, which prevents

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the formation of the dimer. Nevertheless, the energy difference $\Delta E_{\mathrm{HOMO-LUMO}}$ of 2.33 eV (the largest one calculated together with $R^1 = C_6H_4CH_3$) makes this dicationic dinuclear complex the last complex of the series and the least one to be split.

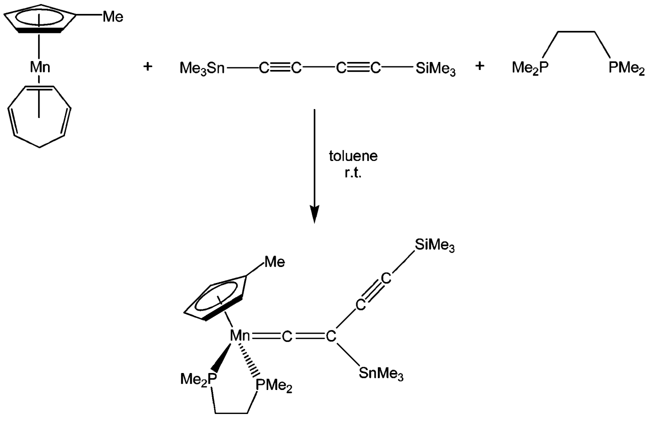
Mononuclear Half-Sandwich Manganese Butatrienylidene Complexes

The butatrienylidene complex has eluded scientists for a long time. These complexes have proven difficult to characterize, the first isolated example being reported in 2000,[86] although unusual dimetallic systems were described in 1999.[150,151] The first example of a mononuclear C_5 complex was described by Dixneuf and co-workers in 1994,[79] followed 2 years later by derivatives containing iridium by Werner and co-workers and group 6 metals by Roth and Fischer.[152−154] A few examples of ruthenium cluster complexes containing butatrienylidenes are also known. However, several groups have reported chemistry that can reasonably be interpreted as proceeding through reactive butatrienylidene intermediates, beginning with the pioneering study by Lomprey and Selegue in 1993.[73] Not surprisingly, given the reactivity of the vinylidene and allenylidene complexes, it has proved challenging to isolate and fully characterize these even more highly unsaturated derivatives, and applications to synthesis are rare to date.

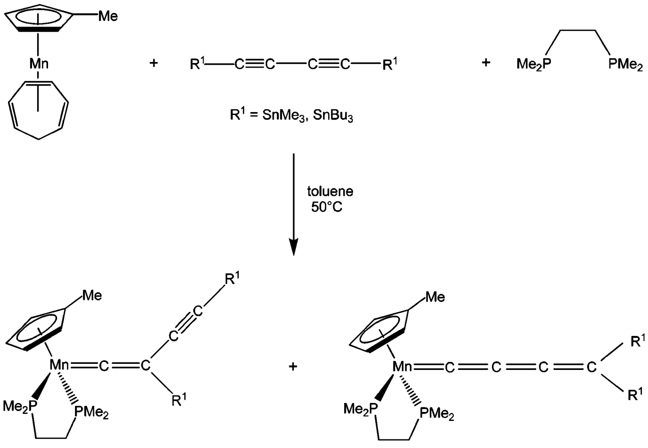
Our interest in this area focuses on the preparation of redox-active di- or polynuclear organometallic complexes containing manganese (end) groups, and we consequently sought to utilize the stability and electron richness of dmpe-substituted half-sandwich Mn^I moieties for the buildup of molecular redox wires.[155] A major route to dinuclear metal systems bearing cumulene bridges utilizes coupling processes of appropriate mononuclear species.[41,45,112,135,156−164] On the basis of the promising results in the synthesis of mononuclear vinylidene complexes described in the preceding section, addition of acetylene derivatives to unsaturated metal complexes was the chosen route to prepare mononuclear half-sandwich manganese butatrienylidene complexes.

(a) Synthesis of Mononuclear Half-Sandwich Manganese Butatrienylidene Complexes. The reaction of $Mn(C_5H_4Me)(\eta^6\text{-cycloheptatriene})$ with $Me_3SiC{\equiv}CC{\equiv}CSnMe_3$ and dmpe gave the corresponding vinylidene species $Mn(C_5H_4Me)(dmpe)({=}C{=}CSnMe_3C{\equiv}CSiMe_3)$ in about 98% yield (Scheme 5). Spectroscopic studies confirmed the observation that only the $SnMe_3$ group migrates to the C_β atom of the vinyl alkynyl chain. The photolysis of the compound $Mn(C_5H_4Me)(dmpe)({=}C{=}C(SnMe_3)C{\equiv}CSiMe_3)$ led to decomposition, and conversion to the corresponding cumulenic complex could not be observed. We replaced the $SiMe_3$ group with the more reactive SnR_3 group, which is known to form radicals in a facile way.

Scheme 5



Scheme 6



Treatment of $Mn(C_5H_4Me)(\eta^6\text{-cycloheptatriene})$ with 1 equiv of dmpe and acetylene derivatives of the type $R^1(C{\equiv}C)_2R^1$ ($R^1 = SnMe_3$, $SnBu_3$) at 50 °C for 3 h gave an inseparable mixture of two complexes, the vinyl alkynyl complex $Mn(C_5H_4Me)(dmpe)({=}C{=}CR^1C{\equiv}CR^1)$ and the corresponding cumulenic complex $Mn(C_5H_4Me)(dmpe)({=}C{=}C{=}C{=}C(R^1)_2)$ (Scheme 6). The mixture was identified using various NMR techniques. Furthermore, suitable crystals for an X-ray diffraction analysis were obtained from one mixture and led to the solid-state structure of the complex $Mn(C_5H_4Me)(dmpe)({=}C{=}C{=}C{=}C(SnMe_3)_2)$.[90] Temperature-dependent studies revealed the fact that these two complexes were not in equilibrium. One could certainly predict that the formation of the vinyl alkynyl complexes is essential for the formation of the cumulenic complexes. The complete transformation could not be accomplished, since the mixture started to decompose under photolytic or thermal conditions.

Since the obtained reaction mixtures of the trimethyltin- and tributyltin-substituted complexes could not be separated, the triphenyltin-substituted butadiyne $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ was used as the starting material under the same conditions. Reactions with $Mn(C_5H_4R')(\eta^6\text{-cycloheptatriene})$ ($R' = H$, Me) and $R''_2PCH_2CH_2PR''_2$ ($R'' = CH_3$ (dmpe), C_2H_5 (depe)) afforded the corresponding vinylidene species $Mn(C_5H_4R')(R''_2$-

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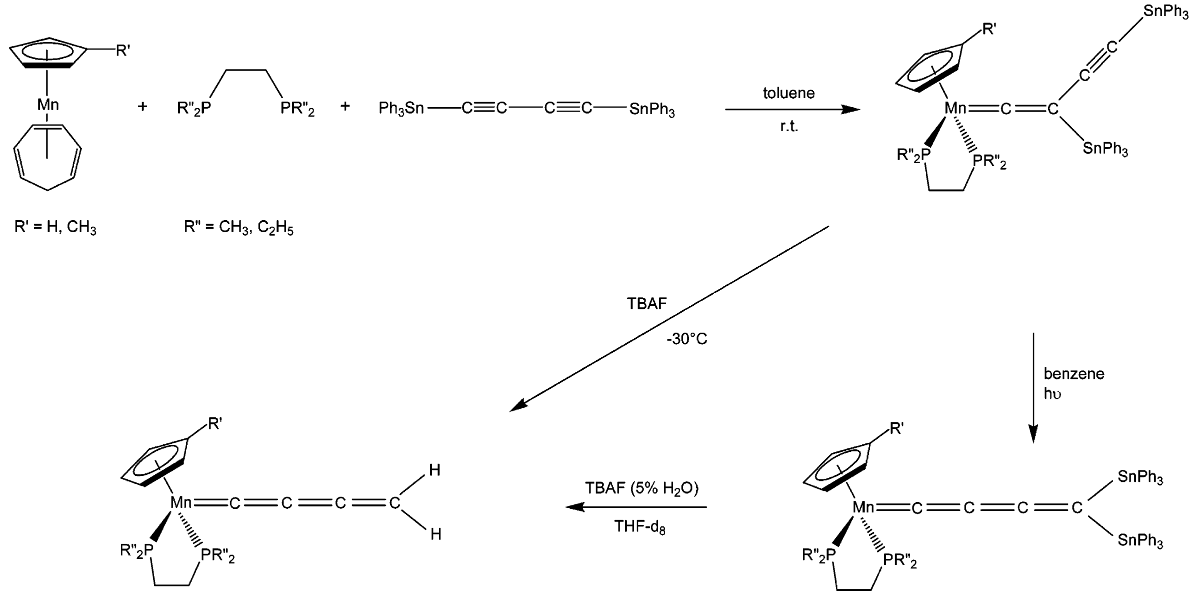
Scheme 7



$PCH_2CH_2PR''_2)(=C=CSnPh_3C\equiv CSnPh_3)$ in about 98% yield (Scheme 7). This reaction required the initial formation of a Mn−alkyne species.[96] However, NMR studies of the reaction carried out in the range of −70 to +20 °C did not reveal any intermediate. When toluene solutions of the vinylidene species were irradiated at 20 °C using a 125 W medium-pressure mercury lamp, the $C_{sp^2}-Sn$ bonds were activated and subsequent transformations into the remarkably stable C_4 cumulene species were observed. The latter were isolated as green solids in approximately 80% yield, and the X-ray structure of $Mn(C_5H_5)(dmpe)(=C=C=C=C(SnPh_3)_2)$ could be obtained from suitable monocrystals (Figure 4).[89]

The complexes $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2)(=C=C=C=C(SnPh_3)_2)$ ($R'' = Me, Et$) constitute the first examples of C_4 metallacumulene species with main-group-metal substituents as end groups, which were assumed to be reactive and were expected to be readily removable. Indeed, deprotection of these species was accomplished with tetrabutylammonium fluoride (TBAF). The parent C_4 cumulenic species $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2)\{=C=C=C=CH_2\}$ ($R' = H, Me$; $R'' = Me, Et$) were formed by selective replacement of the terminal $SnPh_3$ moieties. They were unstable above −5 °C and were therefore characterized in solution at −40 °C. The presence of the terminal CH_2 group was confirmed by ($^1H,^{13}C$) correlation, ^{13}C-DEPT, and $^1H\{^{31}P\}$ decoupling NMR experiments. They are also the first examples of complexes with $[M=C=C=C=CH_2]$ units whose structures have been fully established by NMR spectroscopy in solution. At higher temperatures (−5 °C and above) they decompose to a mixture of as yet unidentified compounds.

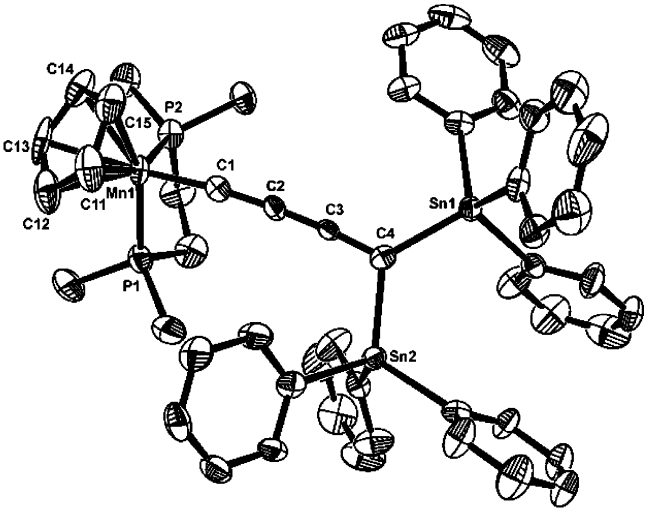
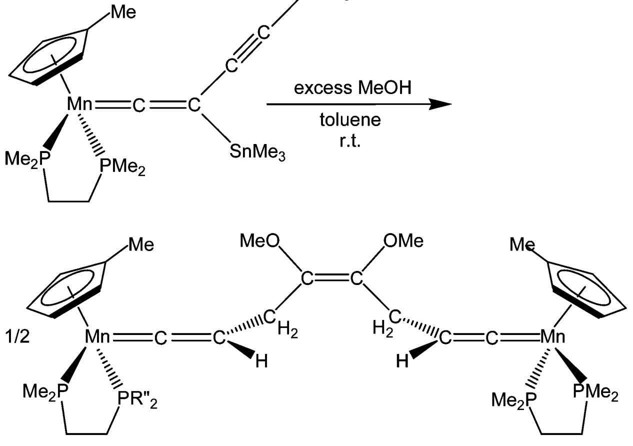


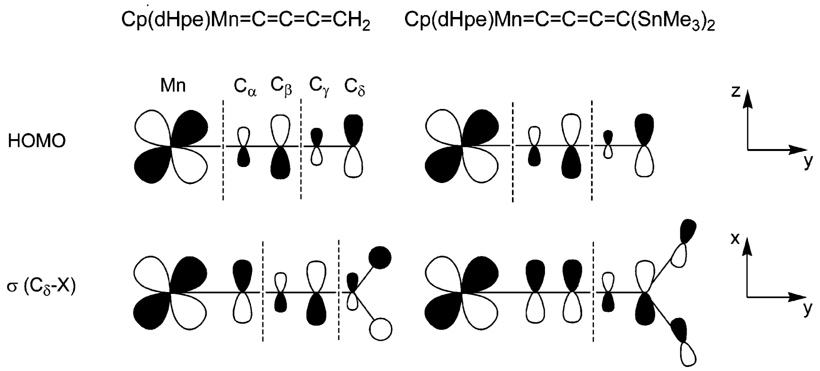
Figure 4. Molecular structure of $Mn(C_5H_5)(dmpe)(=C=C=C=C(SnPh_3)_2)$. Selected bond lengths (Å) and angles (deg): Mn1−C1 = 1.769(4), C1−C2 = 1.296(5), C2−C3 = 1.264(5), C3−C4 = 1.316(5), C4−Sn1 = 2.130(5), C4−Sn2 = 2.132(5); Mn1−C1−C2 = 173.5(4), C2−C3−C4 = 175.5(5), C3−C4−Sn1 = 112.0(3), C3−C4−Sn2 = 122.6(3), Sn1−C4−Sn2 = 124.5(2).

The reactions of the complexes $Mn(C_5H_4Me)(dmpe)(=C=CSnMe_3-C\equiv CSiMe_3)$ and $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2)(=C=CSnPh_3C\equiv CSnPh_3)$ ($R' = H, Me$; $R'' = Me, Et$) with 1 equiv of TBAF (5% H_2O) at −30 °C in THF-d_8 instantaneously led also to the formation of the parent C_4 cumulenic species $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2)\{=C=C=C=CH_2\}$. Although this reaction should proceed via the parent vinyl alkynyl intermediate, the thermodynamically stable product seems to be the cumulenic complex in comparison to the former, due to the faster rate of the 1,2-proton shift. However, the reaction of $Mn(C_5H_4Me)(dmpe)(=C=C(SnMe_3)C\equiv CSiMe_3)$ with an excess of MeOH led to the dinuclear complex $[(C_5H_4Me)(dmpe)\{Mn=C=C(H)=CH_2=C(OCH_3)\}]_2$, formed in high yield (90%) by coupling (Scheme 8). ^{13}C NMR, C−H correlation, long-range C−H, DEPT, and NOE experiments confirmed the

Scheme 8



Scheme 9



dimeric species and also gave a clear indication of a cis arrangement of the two OMe groups. The formation of the dimer involves a 2 + 2 cycloaddition reaction followed by a rearrangement process leading to the coupled product. Similar kinds of coupling reactions have been reported by other groups. However, the exact mechanism still remains to be elucidated.[41,102]

(b) DFT Studies. The effects of terminal substituents on metallacumulene complexes have been studied recently at the DFT level on a series of $(CO)_5Cr({=}C)_nX_2$ (X = F, SiH_3, $CHCH_2$, NH_2, NO_2; $n = 2-8$) complexes.[145] On the basis of calculated bond dissociation energies, the chromium−cumulene bond was shown to be more affected by the amino (decrease of the bond dissociation energies) and nitro substituents (increase of the bond dissociation energies) with π-donor and π-acceptor properties, respectively. As a general conclusion, the authors assumed that even-membered chain metallacumulenes are expected to be stabilized by the presence of π-acceptor substituents. The experimental difference in stability between the C_4 cumulenic complexes with terminal $=CH_2$ groups and the corresponding trialkylltin-substituted complexes led us to a similar study to investigate the influence of the terminal σ-donor SnR_3 by DFT calculations.[87,89] The study was carried out on the model complexes $Mn(C_5H_5)(dHpe)\{=C=C=C=C(SnMe_3)_2\}$ and $Mn(C_5H_5)(dHpe)\{=C=C=C=CH_2\}$. Earlier molecular orbital studies[145,147,148] showed that there are three main orbital interactions between a metal fragment and the C_4H_2 moiety: the cumulene σ orbital donates into the metal d_{z^2} orbital, forming the metal−carbon σ bond, one filled d_π metal orbital back-donates into the empty LUMO of the cumulene unit, and the other filled d_π metal orbital interacts with both the filled HOMO and the empty LUMO+1 of the cumulene to form the HOMO of the complex. Here the HOMOs of both optimized complexes are expectedly π-type orbitals with strong Mn−chain interactions and similar shapes and energies (Scheme 9). These π-type orbitals of the Mn−C_4 chain mainly consist of d_{yz} (Mn) and p_z of the carbon atoms ($C_\alpha-C_\delta$). There are nodal planes between Mn and C_α and between C_β and C_γ, the latter plane being reminiscent of π_2 of a four-centered system. However, the orbital appears strongly polarized through the Mn d_{yz} interaction in such a way that the shape of a nonbonding orbital of a five-centered system is almost reached, in the sense that two nodal planes at C_α and C_γ have "almost" developed (these atoms bear quite small coefficients). However, the HOMOs cannot account for the differences in stability, since no participation of tin or H orbital character is observed.

The stabilizing effect of the tin groups is mirrored in the shape and energy of an occupied molecular orbital in the HOMO region, displaying a bonding interaction in the *xy* plane between the carbon chain and $C_\delta/\sigma_p(Sn)$. It is energetically stabilized (about 1.3 eV) relative to its counterpart in the nonsubstituted complex. The excellent donor properties of the energetically high-lying tin σ orbitals allow out-of-phase $Sn-C_\delta-Sn$ σ-type orbital character to be mixed into a π function of the cumulenic system in a bonding and therefore stabilizing way (Scheme 9

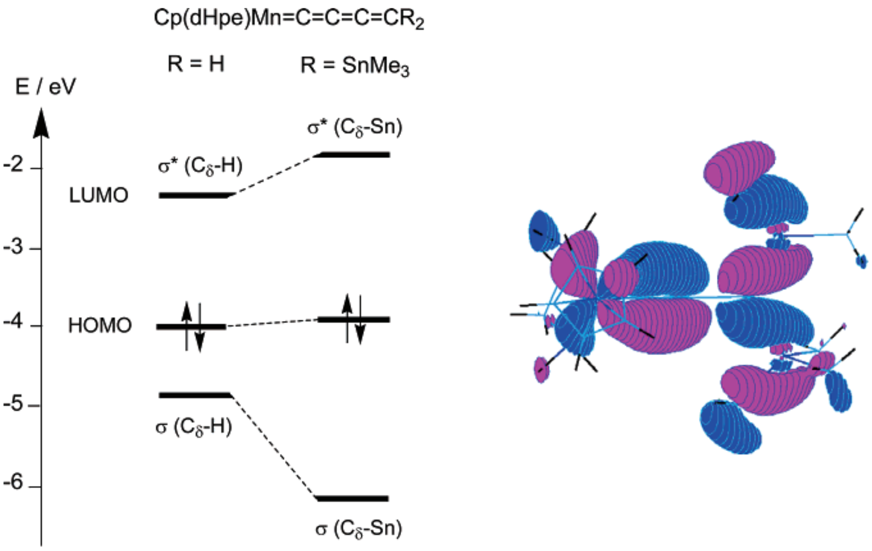


Figure 5. (left) Energy levels of frontier molecular orbitals for the model complexes $Cp(dHpe)Mn{=}C{=}C{=}C{=}CR_2$ (R = H, $SnMe_3$). (right) Calculated occupied MO $\sigma(C_\delta-Sn)$ of $Cp(dHpe)Mn{=}C{=}C{=}C{=}C(SnMe_3)_2$ showing the bonding interactions between C_δ and the terminal tin groups.

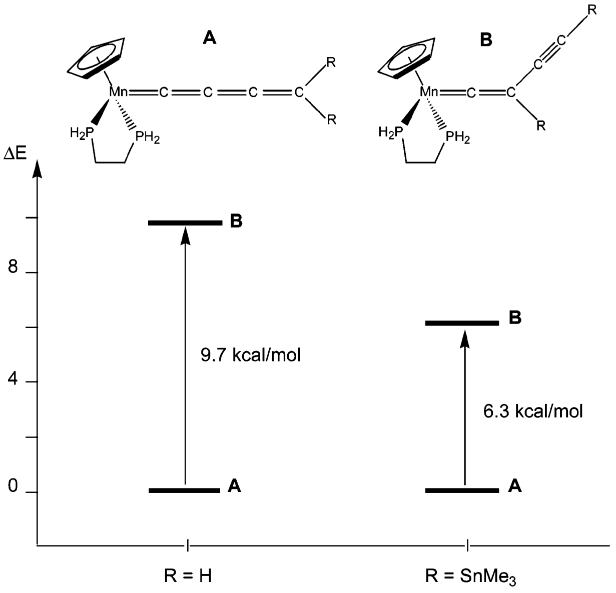
and Figure 5). For complex **35-H** the corresponding $C_\delta H_2$ σ-type orbital character is at much lower energies, which leads to significant contributions of four-electron destabilizing interactions with filled π-orbitals. Overall this electronic destabilization is assumed to be the cause of the instability of the series of parent compounds **29**.

The surprising difference of about 10° observed in the X-ray structures of $(C_5H_4Me)(dmpe)Mn{=}C{=}C{=}C{=}C(SnMe_3)_2$ and $(C_5H_5)(dmpe)Mn{=}C{=}C{=}C{=}C(SnPh_3)_2$ between the terminal bond angles $C3{=}C4{-}Sn$ has also been investigated with DFT calculations.[89] The optimized geometry of the model complex $(C_5H_5)(dHpe)Mn{=}C{=}C{=}C{=}C(SnMe_3)_2$ led to a symmetric ground-state structure with $C{=}C{-}Sn$ bond angles of about 118°. Assuming that the formation of the cumulenic complex involves the radical intermediate $Mn(C_5H_5)(dmpe)({-}C{\equiv}CC{\equiv}CSnPh_3)^\bullet$ from the vinylidene species, the recoordination of the radical group $SnPh_3^\bullet$ can occur on the C_γ atom with an electron π-type orbital perpendicular to the $Mn{-}C{\equiv}CC{\equiv}CSnPh_3$ linear chain. Apparently not much rehybridization occurs then at C_γ. To simulate this rearrangement at its extreme, we performed a linear transit calculation starting from a geometry for $(C_5H_5)(dHpe)Mn{=}C{=}C{=}C{=}C(SnMe_3)_2$ characterized by one $C{=}C{-}Sn$ bond angle fixed at $\alpha = 170°$; the other $C{=}C{-}Sn$ bond angle β and the rest of the geometry were fully optimized. The bending hypersurface with the degree of freedom α showed a relatively flat region in the range of 118−140° ($\Delta E < 3.5$ kcal/mol). Furthermore, the energy difference between the fully optimized symmetric geometry ($\alpha = \beta = 118.2°$) and the geometry simulating the X-ray structure ($\alpha_{fixed} = 125°$; $\beta_{calcd} = 114.6°$) was only 0.4 kcal/mol. These observations therefore support the possibility of $(C_5H_5)(dHpe)Mn{=}C{=}C{=}C{=}C(SnMe_3)_2$ adopting a distorted geometry around C_γ. This distortion could be additionally interpreted in terms of a second-order Jahn−Teller effect with HOMO−LUMO mixing.[103] An attempt to deprotect the vinylidene complex $Mn(C_5H_4Me)(dmpe)({=}C{=}CSnMe_3C{\equiv}CSiMe_3)$ by replacement of the tin and silicon groups with hydrogens using tetrabutylammonium fluoride at −30 °C leads directly to the cumulenic species $Mn(C_5H_4Me)(dmpe)\{{=}C{=}C{=}C{=}CH_2\}$. The formation of the expected vinylidene structure was not observed.

While the $Mn(C_5H_4Me)(dmpe)\{{=}C{=}CHC{\equiv}CH\}$ species seems to be undetectable at −30 °C on the reaction scale, the corresponding tin-substituted vinylidene complexes are sufficiently thermodynamically stable to be fully characterized at room temperature. Then, both isomeric structures have been theoretically investigated with the hydrogen-simplified models $Mn(C_5H_5)(dHpe)\{C_4(SnMe_3)_2\}$ and $Mn(C_5H_5)(dHpe)\{C_4H_2\}$ in terms of total bonding energies. Whatever the substituent H or $SnMe_3$ is, the cumulene species (**A**) are favored over the vinylidene structures (**B**) (Scheme 10) but the energy difference between the **A** and **B** conformations in the case of tin substitution is clearly smaller (6.3 kcal/mol) compared to that for complexes with R = H (9.7 kcal/mol). This calculated thermodynamic destabilization of the vinylidene species when H substituents are involved argue for a strong driving force for its rearrangement to the cumulene structure.

On the basis of the previously described calculations on the oxidative C−C coupling of the $(C_5H_4Me)(dmpe)Mn\{{=}C{=}CR^1R^2\}$ mononuclear species ($R^1 = R^2 = H$; $R^1 = H$, $R^2 = Ph$), we wish to speculate about the possibility of our C_4 cumulene complex to dimerize into a C_8 dinuclear product by oxidation. The mononuclear cationic radical model compound $[(C_5H_5)(dHpe)Mn{=}C{=}C{=}C{=}CH_2]^{\bullet+}$ has been fully optimized with a spin-unrestricted formalism and computed spin densities of $+0.88\alpha$, $+0.31\alpha$, and $+0.35\alpha$ located at the manganese and C_β and C_γ atoms, respectively, which indicate a high probability of finding the unpaired electron on the terminal carbon atom of the C_4 chain. The single-point calculations including a model for solvation effects performed on the gas-phase geometries of the mononuclear cationic radical system and the C−C-coupled dinuclear dicationic product led to a dimerization energy ΔE of +6.0 kcal/mol ($\Delta E = E_{dimer} - 2E_{monomer}$). When these results are compared with those of a previous study on the analogous C_2 oxidatively induced dimerization $2(C_5H_4Me)(dHpe)Mn\{{=}C{=}CH_2\}^{\bullet+} \leftrightarrow (C_5H_4Me)(dHpe)Mn\{{\equiv}CCH_2CH_2C{\equiv}\}Mn(dHpe)(C_5H_4Me)^{2+}$,[87] it appears clear that the formation of the dinuclear dicationic C_8 product is thermodynamically disfavored. Indeed, the spin density on the terminal carbon atom is slightly smaller ($+0.35\alpha$ vs $+0.37\alpha$) compared to that of the C_2 cumulenic cationic radical complex and the formation of the dicationic C_8 dimer is endothermic by 6.0 kcal/mol, while that of the C_4 dimer was previously found to be exothermic by −24.2 kcal/mol, leading to a stable product that was characterized spectroscopically and crystallographically. Nevertheless, a dimerization reaction has been brought to a successful conclusion to $[(C_5H_4Me)(dmpe)\{Mn{=}C{=}C(H){=}CH_2{=}C(OCH_3)\}]_2$ by starting from the vinylidene species $Mn(C_5H_4Me)(dmpe)({=}C{=}CSnMe_3C{\equiv}CSiMe_3)$ with an excess of MeOH, which was already discussed in this context earlier (Scheme 8).

Scheme 10



Conclusions

We believe that the above in-depth study of the manganese vinylidene complexes described in the earlier part of this review highlights the potential of utilizing the ubiquitous C−C bonds in organometallic systems as electron reservoirs, thereby allowing further development of molecular batteries which could find application as components in nanodevices. It is evident that isolation and characterization of complexes containing higher cumulenylidene ligands remains a challenge. It is certain that the next decade will see a rapid development of this area and applications of these complexes in electronic devices.

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